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(54) Title: METHOD AND COMPOSITION FOR PRODUCING SET GYPSUM-CONTAINING PRODUCT WITH INCREASED STRENGTH, RIGIDITY, AND DIMENSIONAL STABILITY

(57) Abstract

The invention provides a method and composition for preparing set gypsum-containing products having increased strength, rigidity, and dimensional stability. The invention concerns making such products by hydration of calcined gypsum in the presence of trimetaphosphate ion to produce set gypsum having the desired characteristics.

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**METHOD AND COMPOSITION FOR PRODUCING  
SET GYPSUM-CONTAINING PRODUCT WITH INCREASED  
STRENGTH, RIGIDITY, AND DIMENSIONAL STABILITY**

5      **Field of the Invention**

This invention relates to a method and composition for preparing set gypsum-containing products, e.g., gypsum boards, reinforced gypsum composite boards, plasters, machinable materials, joint treatment materials, and acoustical tiles. More particularly, the invention concerns 10 making such products by hydration of calcined gypsum in the presence of an additive that causes the set gypsum produced by such hydration to have increased strength, rigidity, and dimensional stability. The additive also provides other improved properties and advantages in preparing the set gypsum-containing products.

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**Background**

Many well known useful products contain set gypsum (calcium sulfate dihydrate) as a significant, and often as the major, component. For example, set gypsum is the major component of paper-faced gypsum 20 boards employed in typical drywall construction of interior walls and ceilings of buildings (see, e.g., U.S. Patents 4,009,062 and 2,985,219). It is also the major component of gypsum/cellulose fiber composite boards and products, as described in U.S. Patent 5,320,677. Products that fill and smooth the joints between edges of gypsum boards often 25 contain major amounts of gypsum (see, e.g., U.S. Patent 3,297,601). Acoustical tiles useful in suspended ceilings can contain significant percentages of set gypsum, as described, for example, in U.S. Patents 5,395,438 and 3,246,063. Traditional plasters in general, e.g., for use to create plaster-surfaced internal building walls, usually depend mainly on

the formation of set gypsum. Many specialty materials, such as a material useful for modeling and mold-making that can be precisely machined as described in U.S. Patent 5,534,059, contain major amounts of gypsum.

5        Most such gypsum-containing products are prepared by forming a mixture of calcined gypsum (calcium sulfate hemihydrate and/or calcium sulfate anhydrite) and water (and other components, as appropriate), casting the mixture into a desired shaped mold or onto a surface, and allowing the mixture to harden to form set (i.e., rehydrated)  
10      gypsum by reaction of the calcined gypsum with the water to form a matrix of crystalline hydrated gypsum (calcium sulfate dihydrate). This is often followed by mild heating to drive off the remaining free (unreacted) water to yield a dry product. It is the desired hydration of the calcined gypsum that enables the formation of an interlocking matrix of  
15      set gypsum crystals, thus imparting strength to the gypsum structure in the gypsum-containing product.

All of the gypsum-containing products described above could benefit if the strength of their component set gypsum crystal structures were increased in order to make them more resistant to the stresses they  
20      may encounter during use.

Also there is a continuing effort to make many such gypsum-containing products lighter in weight by substituting lower density materials (e.g., expanded perlite or air voids) for part of their set gypsum matrix. In such cases there is a need to increase the strength of the set  
25      gypsum above normal levels just to maintain overall product strength at the levels of the previously higher density product, because there is less set gypsum mass to provide strength in the lower density product.

Furthermore, there is a need for greater rigidity in the structure of many of these gypsum-containing products, especially under conditions

of high humidity and temperature. For example, gypsum-containing boards and tiles are often stored or employed in a manner in which they are positioned horizontally. If the set gypsum matrix in these products is not sufficiently rigid, especially under high humidity and temperature, the products may start to sag in areas between the points where they are fastened to or supported by an underlying structure. This can be unsightly and can cause difficulties in use of the products. Thus, there is a continuing need to be able to form set gypsum having increased rigidity.

There is also a need for greater dimensional stability of set gypsum in gypsum-containing products during their manufacture, processing, and commercial application. Especially under conditions of changing temperature and humidity, set gypsum can shrink or expand. For example, moisture taken up in crystal interstices of a gypsum matrix of a gypsum board or tile exposed to high humidity and temperature can aggravate a sagging problem by causing the humidified board to expand. Also, in the preparation of set gypsum products there is usually a significant amount of free (unreacted) water left in the matrix after the gypsum has set. This free water is usually subsequently driven off by mild heating. As the evaporating water leaves the crystal interstices of the gypsum matrix, the matrix tends to shrink from natural forces of the set gypsum (i.e., the water was holding apart portions of the interlocking set gypsum crystals in the matrix, which then tend to move closer together as the water evaporates).

If such dimensional instability could be avoided or minimized, various benefits would result. For example, existing gypsum board production methods would yield more product if the boards did not shrink during drying, and gypsum-containing products desired to be relied on to hold a precise shape and dimensional proportions (e.g., for use in

modeling and mold making) would serve their purposes better. Also, for example, some plasters intended for interior building wall surfaces could benefit from not shrinking during drying, so that the plaster could be applied in thicker layers without danger of cracking, rather than needing 5 to be applied in multiple thinner layers with long pauses to allow adequate drying between layer applications.

Some particular types of gypsum-containing products also exhibit other particular problems. For example, lower density gypsum-containing products are often produced by using foaming agents to create aqueous bubbles in calcined gypsum slurries (flowable aqueous mixtures) that yield corresponding permanent voids in the product when the set gypsum forms. It is often a problem that, because the aqueous foams employed 10 are inherently unstable and therefore many of the bubbles may coalesce and escape the relatively dilute slurry (like bubbles in a bubble bath) before the set gypsum forms, significant concentrations of foaming 15 agents have to be employed to produce the desired concentration of voids in the set gypsum, in order to obtain a product of desired density. This increases costs and risks of adverse effects of chemical foaming agents on other components or properties of the gypsum-containing 20 products. It would be desirable to be able to reduce the amount of foaming agent needed to produce a desired void concentration in set gypsum-containing products.

Thus, there is a continuing need for new and improved compositions and methods for producing set gypsum-containing products 25 that solve, avoid, or minimize all of the problems noted above. The present invention meets this need.

#### Summary of the Invention

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The present inventors have unexpectedly found a composition and method to meet the needs described above. This is accomplished by adding trimetaphosphate ion to a mixture of calcined gypsum and water to be used to produce set gypsum-containing products (as used herein, the term, "calcined gypsum", is intended to mean alpha calcium sulfate hemihydrate, beta calcium sulfate hemihydrate, water-soluble calcium sulfate anhydrite, or mixtures of any or all thereof, and the terms, "set gypsum" and "hydrated gypsum", are intended to mean calcium sulfate dihydrate). When the water in the mixture reacts spontaneously with the calcined gypsum to form set gypsum, the set gypsum is unexpectedly found to have increased strength, rigidity, and dimensional stability, compared with set gypsum formed from a mixture containing no trimetaphosphate ion. The mechanism for these improvements in properties is not understood.

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15 Furthermore, it has been unexpectedly found that trimetaphosphate ion does not retard the rate of the formation of set gypsum from calcined gypsum. In fact, when added at relatively higher concentration levels within its useful ranges of addition, it actually accelerates the rate of hydration of calcined gypsum to form set gypsum.

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This is especially surprising, as is the increase in the strength of the set gypsum, because it has been generally thought in the gypsum art that phosphoric or phosphate materials retard the rate of formation of set gypsum and decrease the strength of the gypsum formed. This is in fact true for most such materials, but not for trimetaphosphate ion.

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Thus, in general, the invention provides a method for producing a set gypsum-containing product having increased strength, rigidity, and dimensional stability, comprising: forming a mixture of calcined gypsum, water, and trimetaphosphate ion, and maintaining the mixture under

conditions (e.g., a temperature preferably less than about 120F) sufficient for the calcined gypsum to convert to set gypsum.

In some embodiments of the invention the method is one of producing a gypsum board comprising a core of set gypsum sandwiched between cover sheets of paper or other material. The board is prepared by forming a flowable mixture (slurry) of calcined gypsum, water, and trimetaphosphate ion, depositing it between cover sheets, and allowing the resultant assembly to set and dry.

While the board thus produced has all of the desired improved properties of increased strength, rigidity, and dimensional stability, it has been observed that, for reasons unknown, when such a board has for some reason become wet or has not been completely dried during production, the bond between the gypsum core and the cover sheets (usually comprising paper) can lose strength or even fail, even when the board contains a typical nonpregelatinized starch (e.g., an acid-modified starch) which normally contributes to better paper-to-core bond integrity. The cover sheets could then delaminate from the board, which would be unacceptable. Fortunately the present inventors have also found a solution to this possible attendant problem. They have found that the problem can be avoided by including a pregelatinized starch in the production slurry. This starch then becomes distributed throughout the resultant gypsum core, and it has been unexpectedly found that this avoids the weakening of the bonding between the core and the cover sheets.

Thus, in some of its embodiments the invention provides a composition and method for producing an even more improved gypsum board. The composition comprises a mixture of water, calcined gypsum, trimetaphosphate ion, and a pregelatinized starch. The method

comprises forming such a mixture, depositing it between cover sheets and allowing the resultant assembly to set and dry.

In cases where it is desired to produce a gypsum board of lighter weight, the invention provides a composition and method for accomplishing this. The composition comprises a mixture of water, calcined gypsum, trimetaphosphate ion, and an aqueous foam, and the method comprises forming such a mixture, depositing it between cover sheets, and allowing the resultant assembly to set and dry. Such composition and method provide a board of lighter weight, because the bubbles of aqueous foam result in corresponding air voids in the set gypsum core of the resultant board. The overall strength of the board is higher than a prior art board produced with the inclusion of an aqueous foam in the mixture, because of the increased strength provided by the inclusion of the trimetaphosphate ion in the mixture used to form the inventive board.

Unexpectedly, there has been found to be another benefit to the inclusion of trimetaphosphate ion in mixtures also containing an aqueous foam. Namely, it has been found that proportionally more air voids (and more overall air void volume) per unit amount of aqueous foam employed, are created in the resultant gypsum-containing product when trimetaphosphate ion is included in the mixture. The reason for this is not known, but the beneficial result is that less foaming agent has to be employed to produce the desired amount of air void volume in the set gypsum-containing product. This in turn results in lower production costs and less risk of adverse effects of chemical foaming agents on other components or properties of the gypsum-containing product.

Aqueous foam and pregelatinized starch can also be included together in compositions and methods of the present invention to provide the combined benefits of both.

In some embodiments the invention provides a composition and method for producing a composite board comprising set gypsum and a reinforcing material. The composition comprises a mixture of calcined gypsum, reinforcing material, and a water-soluble trimetaphosphate salt, which can be mixed with water to produce an inventive mixture of water, calcined gypsum, reinforcing material, and trimetaphosphate ion. The method comprises forming such a mixture, depositing it on a surface, and allowing it to set and dry.

The invention also provides a composition and method for producing a particularly preferred composite product comprising set gypsum and host particles, at least a portion of the set gypsum being positioned in and about accessible voids in the host particles. The composition comprises a mixture of: host particles having accessible voids therein; calcined gypsum, at least a portion of which is in the form of crystals in and about the voids in the host particles; and a water-soluble trimetaphosphate salt. The composition can be mixed with water to produce an inventive mixture of water, host particles having accessible voids therein, calcined gypsum (at least a portion of which is in the form of crystals in and about the voids in the host particles), and trimetaphosphate ion. The method comprises forming such a mixture, depositing it on a surface or into a mold, and allowing it to set and dry.

In some embodiments the invention provides a composition and method for producing a machinable material. The composition comprises a mixture of calcined gypsum, a water-soluble trimetaphosphate salt, a starch, and particles of a water-redispersible polymer. The composition can be mixed with water to produce an inventive mixture of water, calcined gypsum, trimetaphosphate ion, starch, and particles of water-redispersible polymer. The method comprises forming such a mixture, depositing it on a surface or into a mold, and allowing it to set and dry.

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In some embodiments the invention provides a composition and method for producing a material employed to finish a joint between edges of gypsum boards. The composition comprises a mixture of calcined gypsum, a water-soluble trimetaphosphate salt, a binder, a thickener, and a non-leveling agent. The composition can be mixed with water to produce an inventive mixture of calcined gypsum, trimetaphosphate ion, binder, thickener, and non-leveling agent. The method comprises forming such a mixture, inserting it into a joint between edges of gypsum boards, and allowing it to set and dry.

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In some embodiments the invention provides a composition and method for producing an acoustical tile. The composition comprises a mixture of water, calcined gypsum, trimetaphosphate ion, a gelatinized starch, and mineral wool or paper fiber. The method comprises forming such a mixture, casting it into a tray, and allowing it to set and dry.

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In some embodiments the invention provides a composition and method for producing another type of acoustical tile. The composition comprises a mixture of water, calcined gypsum, trimetaphosphate ion, a gelatinized starch, expanded perlite particles, and a fiber reinforcing agent. The method comprises forming such a mixture, casting it into a tray, and allowing it to set and dry.

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#### Description of Preferred Embodiments

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The present invention can be practiced employing compositions and methods similar to those employed in the prior art to prepare various set gypsum-containing products. The essential difference in the compositions and methods of this invention from compositions and methods employed in the prior art to prepare various set gypsum-containing products is that a water-soluble trimetaphosphate salt is included to provide that in methods of the invention the rehydration of

calcined gypsum to form set gypsum takes place in the presence of trimetaphosphate ion and thereby produces the benefits of the invention. In other respects the compositions and methods of the invention can be the same as the corresponding compositions and methods of the prior  
5 art.

The trimetaphosphate salt included in compositions of the invention can comprise any water-soluble trimetaphosphate salt that does not adversely interact with other components of the composition. Some examples of useful salts are sodium trimetaphosphate, potassium  
10 trimetaphosphate, ammonium trimetaphosphate, lithium trimetaphosphate, and mixed salts thereof, among others. Sodium trimetaphosphate is preferred. It is readily commercially available, for example, from Monsanto Company of St. Louis, Missouri.

To be used in the practice of methods of the invention, the trimetaphosphate salt is dissolved in the aqueous mixture of calcined gypsum to yield a trimetaphosphate ion concentration of from about 0.004 to about 2.0 percent by weight, based on the weight of the calcined gypsum. A preferred concentration of trimetaphosphate ion is from about 0.04 to about 0.16 percent. A more preferred concentration is about 0.08  
15 percent. If desired for easier storage and delivery in the practice of some embodiments of the invention, the trimetaphosphate salt can be predissolved in water and inserted into the mixture in the form of an aqueous solution.  
20

In accordance with the invention, the trimetaphosphate ion need  
25 only be present in the aqueous mixture of calcined gypsum during the hydration of the calcined gypsum to form set gypsum. Therefore, while it is usually most convenient and thus preferred to insert the trimetaphosphate ion into the mixture at an early stage, it is also sufficient to insert the trimetaphosphate ion into the mixture of calcined gypsum

and water at a somewhat later stage. For example, in preparing typical gypsum boards, water and calcined gypsum are brought together in a mixing apparatus, are mixed thoroughly, and then are usually deposited onto a cover sheet on a moving belt, and a second cover sheet is placed over the deposited mixture before the major part of the rehydration of calcined gypsum to form set gypsum occurs. While it is most convenient to get the trimetaphosphate ion into the mixture during its preparation in the mixing apparatus, it is also sufficient to add the trimetaphosphate ion at a later stage, e.g., by spraying an aqueous solution of the ion onto the deposited aqueous mixture of calcined gypsum just before the second cover sheet is placed over the deposit, so that the aqueous trimetaphosphate ion solution will soak into the deposited mixture and be present when the bulk of the hydration to form set gypsum occurs.

Other alternative methods of getting the trimetaphosphate ion into the mixture will be apparent to those of ordinary skill in the art and are of course considered to be within the scope of the present invention. For example, it may be possible to pre-coat one or both of the cover sheets with a trimetaphosphate salt, so that the salt will dissolve and cause trimetaphosphate ion to migrate through the mixture when the deposit of the aqueous mixture of calcined gypsum comes into contact with the cover sheet. Another alternative is to mix a trimetaphosphate salt with raw gypsum even before it is heated to form calcined gypsum, so that the salt is already present when the calcined gypsum is mixed with water to cause rehydration.

The calcined gypsum employed in the invention can be in the form and concentrations typically found useful in the corresponding embodiments of the prior art. It can be alpha calcium sulfate hemihydrate, beta calcium sulfate hemihydrate, water-soluble calcium sulfate anhydrite, or mixtures of any or all thereof, from natural or

synthetic sources. In some preferred embodiments alpha calcium sulfate hemihydrate is employed for its yield of set gypsum having relatively high strength. In other preferred embodiments beta calcium sulfate hemihydrate or a mixture of beta calcium sulfate hemihydrate and water-soluble calcium sulfate anhydrite are employed.

Other conventional additives can be employed in the practice of the invention in customary amounts to impart desirable properties and to facilitate manufacturing, such as, for example, aqueous foam, set accelerators, set retarders, recalcination inhibitors, binders, adhesives, dispersing aids, leveling or nonleveling agents, thickeners, bactericides, fungicides, pH adjusters, colorants, reinforcing materials, fire retardants, water repellants, fillers and mixtures thereof.

In inventive embodiments wherein the method and composition are for preparing gypsum board comprising a core of set gypsum-containing material sandwiched between cover sheets, trimetaphosphate ion is employed in the concentrations and manner described above. In other respects, the composition and method can be practiced with the same components and in the same manner as the corresponding compositions and methods for preparing gypsum board of the prior art, for example, as described in US Patents 4,009,062 and 2,985,219, the disclosures of which are incorporated herein by reference. Boards produced using the inventive composition and method exhibit improved strength, rigidity, and dimensional stability.

In preferred methods and compositions for preparing gypsum board, wherein the surface sheets of the board comprise paper, a pregelatinized starch is also employed to avoid the otherwise slightly increased risk of paper delamination under conditions of extreme moisture. Pregelatinizing of raw starch is achieved by cooking in water at temperatures of at least 185F or by other well known methods.

Some examples of readily available pregelatinized starches that serve the purposes of the present invention are (identified by their commercial names): PCF1000 starch, available from Lauhoff Grain Co.; and AMERIKOR 818 and HQM PREGEL starches, both available from Archer Daniels Midland Co.

To be used in the practice of the invention, the pregelatinized starch is included in the aqueous mixture of calcined gypsum at a concentration of from about 0.08 to about 0.5 percent by weight, based on the weight of the calcined gypsum. A preferred concentration of pregelatinized starch is from about 0.16 to about 0.4 percent. A more preferred concentration is about 0.3 percent. If the corresponding embodiment of the prior art also contains a starch that has not been pregelatinized (as many do), the pregelatinized starch in the inventive embodiment can also serve to replace all or a portion of the amount of that prior art starch normally employed.

In embodiments of the invention that employ a foaming agent to yield voids in the set gypsum-containing product to provide lighter weight, any of the conventional foaming agents known to be useful in preparing foamed set gypsum products can be employed. Many such foaming agents are well known and readily available commercially, e.g., from GEO Specialty Chemicals in Ambler, Pennsylvania. For further descriptions of useful foaming agents, see, for example: U.S. Patents 4,676,835; 5,158,612; 5,240,639 and 5,643,510; and PCT International Application Publication WO 95/16515, published June 22, 1995.

In many cases it will be preferred to form relatively large voids in the gypsum product, in order to help maintain its strength. This can be accomplished by employing a foaming agent that generates foam that is relatively unstable when in contact with calcined gypsum slurry. Preferably, this is accomplished by blending a major amount of foaming

agent known to generate relatively unstable foam, with a minor amount of foaming agent known to generate relatively stable foam.

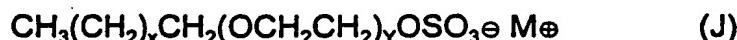
Such a foaming agent mixture can be pre-blended "off-line", i.e., separate from the process of preparing foamed gypsum product.  
5 However, it is preferable to blend such foaming agents concurrently and continuously, as an integral "on-line" part of the process. This can be accomplished, for example, by pumping separate streams of the different foaming agents and bringing the streams together at, or just prior to, the foam generator that is employed to generate the stream of aqueous foam  
10 which is then inserted into and mixed with the calcined gypsum slurry. By blending in this manner, the ratio of foaming agents in the blend can be simply and efficiently adjusted (for example, by changing the flow rate of one or both of the separate streams) to achieve the desired void characteristics in the foamed set gypsum product. Such adjustment will  
15 be made in response to an examination of the final product to determine whether such adjustment is needed. Further description of such "on-line" blending and adjusting can be found in U.S. Patent 5,643,510, and in copending U.S. Patent Application 08/577,367, filed Dec. 22, 1995.

An example of one type of foaming agent, useful to generate  
20 unstable foams, has the formula



wherein R is an alkyl group containing from 2 to 20 carbon atoms, and M is a cation. Preferably, R is an alkyl group containing from 8 to 12 carbon atoms.

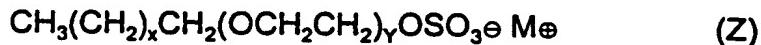
25 An example of one type of foaming agent, useful to generate stable foams, has the formula



wherein X is a number from 2 to 20, Y is a number from 0 to 10 and is greater than 0 in at least 50 weight percent of the foaming agent, and M is a cation.

5 In some preferred embodiments of the invention, foaming agents having the formulas (Q) and (J) above are blended together, such that the formula (Q) foaming agent and the portion of the formula (J) foaming agent wherein Y is 0, together constitute from 86 to 99 weight percent of the resultant blend of foaming agents.

10 In some preferred embodiments of the invention, the aqueous foam has been generated from a pre-blended foaming agent having the formula



wherein X is a number from 2 to 20, Y is a number from 0 to 10 and is 0 in at least 50 weight percent of the foaming agent, and M is a cation.

15 Preferably, Y is 0 in from 86 to 99 weight percent of the formula (Z) foaming agent.

20 In inventive embodiments wherein the method and composition are for preparing a composite board comprising set gypsum and particles of a reinforcing material, trimetaphosphate ion is employed in the concentrations and manner described above. It is particularly preferred that the composite product comprise set gypsum and host particles, at least a portion of the set gypsum being positioned in and about accessible voids in the host particles. The inventive composition comprises a mixture of: host particles having accessible voids therein; calcined gypsum, at least a portion of which is in the form of crystals in and about the voids in the host particles; and a water-soluble trimetaphosphate salt. The composition can be mixed with water to produce an inventive mixture of water, host particles having accessible voids therein, calcined gypsum (at least a portion of which is in the form

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of crystals in and about the voids in the host particles), and trimetaphosphate ion. The method comprises forming such a mixture, depositing it on a surface or into a mold, and allowing it to set and dry. In other respects, the composition and method can be practiced with the  
5 same components and in the same manner as the corresponding compositions and methods for preparing composite board of the prior art, for example, as described in US Patent 5,320,677, the disclosure of which is incorporated herein by reference.

In inventive embodiments wherein the method and composition  
10 are for preparing a machinable material, trimetaphosphate ion is employed in the concentrations and manner described above. In some preferred forms of such embodiments the composition comprises a mixture of calcined gypsum, a water-soluble trimetaphosphate salt, a starch, and particles of a water-redispersible polymer. The composition  
15 can be mixed with water to produce an inventive mixture of water, calcined gypsum, trimetaphosphate ion, starch, and particles of water-redispersible polymer. The method comprises forming such a mixture, depositing it on a surface or into a mold, and allowing it to set and dry. In respect to aspects other than the inclusion of trimetaphosphate salts  
20 and ions, the composition and method can be practiced with the same components and in the same manner as the corresponding compositions and methods for preparing machinable plaster material of the prior art, for example, as described in US Patent 5,534,059, the disclosure of which is incorporated herein by reference.

In inventive embodiments wherein the method and composition  
25 are for producing a material employed to finish a joint between edges of gypsum boards, trimetaphosphate salt or ion is employed in the concentrations described above. In respect to aspects other than the inclusion of trimetaphosphate salts and ions, the composition and method

can be practiced with the same components and in the same manner as the corresponding compositions and methods for producing a joint finishing material in the prior art, for example, as described in US Patent 3,297,601, the disclosure of which is incorporated herein by reference.

- 5 In some preferred forms of such embodiments the composition comprises a mixture of calcined gypsum, a water-soluble trimetaphosphate salt, a binder, a thickener, and a non-leveling agent. The composition can be mixed with water to produce an inventive mixture of calcined gypsum, trimetaphosphate ion, binder, thickener, and non-  
10 leveling agent. The method comprises forming such a mixture, inserting it into a joint between edges of gypsum boards, and allowing it to set and dry.

In such preferred joint finishing embodiments the binder, thickener, and non-leveling agent are chosen from the components well known to those skilled in the joint compound art. For example, the binder can be a conventional latex binder, with poly(vinyl acetate) and poly(ethylene-co-vinyl acetate) being preferred and being included in a range of from about 1 to about 15 percent by weight of the composition. An example of a useful thickener is a cellulosic thickener, e.g., ethylhydroxy ethylcellulose, hydroxypropyl methylcellulose, methylhydroxypropyl cellulose, or hydroxyethyl cellulose, included in a range of from about 0.1 to about 2 percent by weight of the composition. Examples of suitable non-leveling agents are attapulgite, sepiolite, bentonite, and montmorillonite clays, included in a range of from about 1 to about 10 percent by weight of the  
20 composition.  
25

In inventive embodiments wherein the method and composition are for preparing an acoustical tile, trimetaphosphate ion is included in the concentrations described above. In some preferred forms of such embodiments the composition comprises a mixture of water, calcined

gypsum, trimetaphosphate ion, a gelatinized starch, and mineral wool or a mixture of water, calcined gypsum, trimetaphosphate ion, a gelatinized starch, expanded perlite particles, and a fiber reinforcing agent. The method comprises forming such a mixture, casting it into a tray, and allowing it to set and dry. In respect to aspects other than the inclusion of trimetaphosphate ion, the composition and method can be practiced with the same components and in the same manner as the corresponding compositions and methods for producing an acoustical tile of the prior art, for example, as described in US Patents 5,395,438 and 10 3,246,063, the disclosures of which are incorporated herein by reference.

The following examples are presented to further illustrate some preferred embodiments of the invention and to compare them with methods and compositions outside the scope of the invention. Unless otherwise indicated, concentrations of materials in compositions and mixtures are given in percent by weight based upon the weight of calcined gypsum present. The abbreviation, "STMP", stands for sodium trimetaphosphate, and the abbreviation, "TMP", stands for trimetaphosphate.

20

#### EXAMPLE 1

##### Laboratory Cube Compressive Strength

Samples of gypsum-containing products were prepared in accordance with the invention and compared, in regard to compressive strength, with samples prepared using methods and compositions 25 outside the scope of the invention. The test procedure employed was in accordance with ASTM C472-93.

Samples were prepared by dry blending: 500g of beta calcium sulfate hemihydrate; 0.6g of a set accelerator referred to as CSA (Climate Stable Accelerator) commercially available from United States

5

Gypsum Company and comprising fine ground particles of calcium sulfate dihydrate coated to maintain efficiency; and 0g additive (control samples), 0.5-2g of STMP (inventive samples), or 0.5-2g of other phosphate additives (comparative samples). The samples were then mixed with 700ml tap water having a temperature of 70F in a 2 liter WARING blender, allowed to soak for 5 seconds and mixed at low speed for 10 seconds. The slurries thus formed were cast into molds to prepare cubes (2 inches per side). After the calcium sulfate hemihydrate set to form gypsum (calcium sulfate dihydrate), the cubes were removed from the molds and dried in a ventilated oven at 112F for at least 72 hours or until their weight stopped changing. The dried cubes had a density of about 44 pounds per cubic foot (pcf).

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Each dry cube's compressive strength was measured on a SATEC testing machine. Results are reported in TABLE 1, below, as average values of three tested samples. Strength values for control samples varied, because various sources of beta calcium sulfate hemihydrate and/or different batches of beta calcium sulfate hemihydrate were employed. Results in the table are reported in the form of the measured compressive strength in pounds per square inch (psi) and percent change in strength over the relevant control (%Δ). Measured values are estimated to have an experimental error of about +/- 5% (thus, a reported strength increase over the control of 10% may have actually been anywhere in the range of 5-15%).

20

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TABLE 1  
Compressive Strength

	Additive	0% additive (psi)	0.1% additive (psi; %Δ)	0.2% additive (psi; %Δ)	0.4% additive (psi; %Δ)	0.8% additive (psi; %Δ)
5	STMP	987	1054; 6.8	1075; 8.9	1072; 8.6	-----
	STMP	724	843; 16.4	957; 32.2	865; 19.5	783; 8.1
	STMP	742	819; 10.4	850; 14.6	-----	-----
	STMP	714	800; 12.0	834; 16.8	-----	-----
10	STMP	842	985; 17.0	1005; 19.4	1053; 25.1	611; -27.4
	STMP	682	803; 17.7	826; 21.1	887; 30.1	-----
	sodium phosphate	950	951; 0.1	929; -2.2	-----	-----
15	sodium tripoly-phosphate	950	993; 4.5	873; -8.1	-----	-----
	sodium hexameta-phosphate	950	845; -11.1	552; -41.9	-----	-----
	dicalcium phosphate	763	769; 0.8	775; 1.6	761; -0.3	-----
20	disodium phosphate	763	757; -0.8	728; -4.6	700; -8.3	-----
	monocalcium phosphate monohydrate	763	786; 3.0	766; 0.4	824; 8.0	-----
25						

The data in TABLE 1 illustrate that the inventive samples (STMP) generally exhibited significantly increased strength over the controls, while the noninventive comparative samples generally showed very little or no strength increase or even a significant strength decrease.

EXAMPLE 2

Rigidity (Laboratory Gypsum Board Sag Resistance)

Samples of gypsum-containing boards were prepared in a laboratory in accordance with the invention and compared, in regard to rigidity, with sample boards prepared using methods and compositions outside the scope of the invention.

5 Samples were prepared by mixing in a 5 liter WARING blender for 10 seconds at low speed: 1.5kg of beta calcium sulfate hemihydrate; 2g of CSA set accelerator; 2 liters of tap water; and 0g additive (control samples), 3g of STMP (inventive samples), or 3g of other additives (comparative samples). The slurries thus formed were cast into trays to prepare flat gypsum board samples, each having dimensions of about 6x24x½ inches. After the calcium sulfate hemihydrate set to form gypsum (calcium sulfate dihydrate), the boards were dried in a 112F oven until their weight stopped changing. The final measured weight of 10 each board was recorded. No paper facing was applied to these boards, in order to avoid the effect of paper covers on the gypsum boards' sag 15 performance under humidified conditions.

15 Each dried board was then laid in a horizontal position upon two ½-inch-wide supports whose length extended the full width of the board, 20 with one support at each end of the board. The boards remained in this position for 4 days under continuous surrounding conditions of 90F temperature and 90 percent relative humidity. The extent of sag of the board was then determined by measuring the distance (in inches) of the center of the top surface of the board from the imaginary horizontal plane 25 extending between the top edges of the ends of the board. The rigidity of the set gypsum matrix of the board is considered to be inversely proportional to the extent of the sag of the board. Thus, the greater the extent of the sag is, the lower is the relative rigidity of the set gypsum matrix comprising the board.

5

The results of the rigidity tests are reported in TABLE 2, including the composition and concentration (weight percent based on the weight of calcium sulfate hemihydrate) of the additive, the final weight of the board , and the extent of measured sag. The additives employed in the comparative samples (outside the scope of the invention) are representative of other materials that have been employed to attempt to improve resistance of gypsum board to sagging under conditions of high humidity.

10

**TABLE 2**  
**Extent of Gypsum Board Sag**

15

20

Additive	Additive (weight %)	Board Weight (g)	Board Sag (inches)
none (control)	0	830	0.519
STMP	0.2	838	0.015
boric acid	0.2	829	0.160
sodium aluminum phosphate	0.2	835	0.550
wax emulsion	7.5	718	0.411
glass fiber	0.2	838	0.549
glass fiber + boric acid	0.2 + 0.2	825	0.161

25

The data in TABLE 2 illustrate that the board (STMP) prepared in accordance with the invention was much more resistant to sag (and thus much more rigid) than the control board and the noninventive comparative boards.

### **EXAMPLE 3**

#### **Gypsum Board Nail Pull Resistance**

5

Laboratory prepared samples of typical paper-covered gypsum boards produced in accordance with the invention were compared with control boards in regard to nail pull resistance. Nail pull resistance is a measure of a combination of the strengths of the board's gypsum core, its paper cover sheets, and the bond between the paper and the gypsum. The test measures the maximum force required to pull a nail with a head through the board until major cracking of the board occurs, and is carried out in accordance with ASTM C473-95.

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Slurries were prepared by mixing in a HOBART mixer for 40 seconds at a medium speed: 3.0 kg of beta calcium sulfate hemihydrate; 5g of CSA set accelerator; 10g of LC-211 starch (a dry-milled acid-modified non-pregelatinized wheat starch typically included in prior art formulations for gypsum board and commercially available from Archer Daniels Midland Milling Co.); 20g of fine hammermilled paper fiber; 3 liters of tap water; 0-6g of STMP; and 0-30g of PCF1000 pregelatinized corn starch, commercially available from Lauhoff Grain Co.

The slurries thus formed were cast into trays on top of paper and then had paper applied to their top surface to prepare flat gypsum board samples, each having dimensions of about 6x24x $\frac{1}{2}$  inches. The paper on one surface was multi-ply with manila outer plies, and the paper on the other surface was multi-ply newsline, both typical of papers employed to prepare paper-covered gypsum board in the board industry. Each board was then held in a 350F oven until it lost 25 percent weight and was then transferred to and held in a 112F oven until it reached constant weight.

Final board weight and nail pull resistance were measured. The results are reported in TABLE 3.

TABLE 3  
Nail Pull Resistance

	STMP Concentration (weight %)	PCF1000 Starch (weight %)	Board Weight (lbs/1000ft <sup>2</sup> )	Nail Pull Resistance (lbs)
5	0	0	2465	150
	0.1	0	2454	155
	0.2	0	2326	158
	0.1	0.5	2458	168
	0.2	1.0	2495	176

The results in TABLE 3 show that boards prepared in accordance with the invention exhibited higher overall strength (nail pull resistance) compared with control boards.

15

#### EXAMPLE 4

##### Dimensional Stability and Rigidity of Production Line Gypsum Board

Paper-covered foamed gypsum boards were prepared on a typical full scale production line in a commercial gypsum board manufacturing facility. Boards were prepared with various concentrations of trimetaphosphate ion and were compared with control boards (prepared without trimetaphosphate ion) in regard to dimensional stability and rigidity. Except for the inclusion of trimetaphosphate ion in the preparation of some of the boards, the boards were prepared using methods and ingredients typical of prior art gypsum board production methods and ingredients. The ingredients and their approximate weight percentages (expressed as relatively narrow ranges based upon the weight of calcined gypsum employed) are listed in TABLE 4.

TABLE 4  
Gypsum Board Production Ingredients

	INGREDIENT	WEIGHT %
5	beta calcium sulfate hemihydrate	100
	water	94 - 98
10	set accelerator	1.1 - 1.6
	starch	0.5 - 0.7
	dispersant	0.20 - 0.22
	paper fiber	0.5 - 0.7
	set retarder	0.07 - 0.09
	foaming agent	0.02 - 0.03
	sodium trimetaphosphate	0 - 0.16
	recalcination inhibitor	0.13 - 0.14

- 15            In TABLE 4: the set accelerator comprised finely ground sugar-coated particles of calcium sulfate dihydrate produced by United States Gypsum Company and referred to as "HRA" (which stands for heat resistant accelerator); the starch was dry-milled acid-modified HI-BOND starch obtained commercially from Lauhoff Grain Co.; the dispersant was  
 20            DILOFLO, a naphthalene sulfonate obtained commercially from GEO Specialty Chemicals of Ambler, Pennsylvania; the paper fiber was fine hammermilled paper fiber; the set retarder was VERSENEX 80, a chelating agent obtained commercially from Van Walters & Rogers of Kirkland, Washington; the foaming agent was WITCOLATE1276, obtained commercially from Witco Corp. of Greenwich, Connecticut; the sodium trimetaphosphate was supplied commercially by Monsanto Co. of St. Louis, Missouri; and the recalcination inhibitor was CERELOSE
- 25

2001, a dextrose employed to reduce recalcination of board ends during drying.

The boards were produced on a four foot wide continuous production line by: continuously introducing and mixing the ingredients in a mixer to form an aqueous slurry (the foaming agent was used to generate aqueous foam in a separate foam generating system; the foam was then introduced into the slurry through the mixer); continuously depositing the slurry on a paper cover sheet (face paper) on a moving belt; placing another paper cover sheet (back paper) over the deposited slurry to form  $\frac{1}{2}$  inch thick board; when the hydration of the calcium sulfate hemihydrate to form calcium sulfate dihydrate proceeded far enough to make the slurry hard enough to cut precisely, cutting the moving board to make individual boards of about 12x4 feet and  $\frac{1}{2}$  inch thick; and drying the boards in a heated multideck kiln.

Rigidity of the boards was then determined by measuring sag as described in Example 2, except that the boards tested were about 1x4 foot (the 1 foot being in the production line direction) sections cut from the production boards. Measurement of sag was carried out after conditioning the boards in an environment of 90F temperature and 90% relative humidity for 24, 48, and 96 hours. Results are reported in TABLE 5 for inventive samples produced with various concentrations of trimetaphosphate ion and control samples (0% sodium trimetaphosphate) produced immediately before and after the inventive samples.

TABLE 5  
Production Line Gypsum Board Sag

STMP Concentration (weight %)	Board Sag after 24hrs. (inches)	Board Sag after 48hrs. (inches)	Board Sag after 96hrs. (inches)
5	0 (before)	3.45	3.95
	0.004	3.23	3.71
	0.008	2.81	3.31
	0.016	1.72	1.91
	0.024	0.96	1.12
	0.04	0.49	0.68
	0.08	0.21	0.24
	0 (after)	3.65	4.58
10			6.75

15           The data in TABLE 5 illustrate that the boards prepared in accordance with the invention were progressively more resistant to sag (and thus progressively more rigid) than the control boards, as STMP concentration was increased.

20           Both wet 12x4ft. production boards and final dried 12x4ft. production line boards were also measured (in accordance with ASTM C473-95) to determine the amounts of shrinkage of their widths and lengths after drying. The more the boards shrink, the less is their dimensional stability. The results are reported in TABLE 6.

25

TABLE 6  
Production Line Gypsum Board Shrinkage

	STMP Concentration (weight %)	Board Width Shrinkage (inches/4ft.)	Board Length Shrinkage (inches/12ft.)
5	0 (control)	0.13	0.38
	0.004	0.06	0.38
	0.008	0	0.31
	0.016	0	0.25
10	0.024	0	0.25
	0.040	0	0
	0.080	0	0
	0.16	0	0

15           The data in TABLE 6 show that boards prepared in accordance with the invention were more dimensionally stable than control boards. At 0.04% STMP addition and above, no length or width shrinkage was found.

20

#### EXAMPLE 5

##### Production Line Gypsum Board Nail Pull Resistance

Another set of paper-covered foamed gypsum boards was prepared on a typical full scale production line in a gypsum board manufacturing facility. Boards were prepared with three concentrations of trimetaphosphate ion and were compared with control boards (prepared without trimetaphosphate ion) in regard to nail pull resistance.

25

Except for the inclusion of trimetaphosphate ion in the preparation of some of the boards, the boards were prepared using methods and

ingredients typical of prior art gypsum board production methods and ingredients. The ingredients and their weight percentages were the same as those listed in TABLE 4 above. The method of preparation of the boards was as described in EXAMPLE 4.

5 Nail pull resistance was determined in accordance with ASTM C473-95. Results are reported in TABLE 7 for inventive samples produced with various concentrations of trimetaphosphate ion and control samples (0% sodium trimetaphosphate) produced immediately before and after the inventive samples.

10

TABLE 7  
Production Line Gypsum Board Nail Pull Resistance

15	STMP Concentration (weight %)	Nail Pull Resistance (lbs)
20	0 (before)	89
	0.04	93
	0.08	96
	0.16	99
	0 (after)	90

The results in TABLE 7 show that production boards prepared in accordance with the invention exhibited higher overall strength (nail pull resistance) compared with control boards.

25

EXAMPLE 6Production Line Gypsum Board Paper Bond Integrity

Another set of paper-covered foamed gypsum boards was prepared on a typical full scale production line in a gypsum board manufacturing facility. Boards were prepared with various concentrations of trimetaphosphate ion, pregelatinized starch, and non-pregelatinized starch and were compared with control boards (prepared without trimetaphosphate ion or pregelatinized starch) in regard to the integrity of the bond between the gypsum board core and its face cover paper after conditioning under extremely wet and humidified conditions.

Except for the inclusion of trimetaphosphate ion and pregelatinized starch and the varying of the concentration of non-pregelatinized starch in the preparation of some of the boards, the boards were prepared using methods and ingredients typical of prior art gypsum board production methods and ingredients. The ingredients and their weight percentages were the same as those listed in TABLE 4 above. The method of preparation of the boards was as described in EXAMPLE 4.

The pregelatinized starch employed in the tests was PCF1000, commercially available from Lauhoff Grain Co. The non-pregelatinized starch was HI-BOND, a dry-milled acid-modified non-pregelatinized starch commercially available from Lauhoff Grain Co.

After production line preparation of the boards, samples with dimensions of 4x6x $\frac{1}{2}$  inches (the 4 inches being in the production line direction) were cut from the boards. Each of these smaller board samples was then conditioned by keeping the total area of the outer surface of the cover paper on its face side in contact with a fully water-soaked cloth for about 6 hours in an environment of 90F temperature and 90 percent relative humidity and then removing the wet cloth and allowing the board sample to slowly dry in that same environment until it reached

constant weight (usually about 3 days). A one eighth inch-deep straight score was then made in the rear surface of the board sample 2½ inches from and parallel to one of the 6 inch edges. The board core was then snapped along the score without breaking or stressing the paper on the face side of the board, and the larger (2½x6 inches) piece of the board sample was then rotated and forced downward while the smaller piece was held stationary and horizontally with its rear surface up, in an attempt to force the face paper on the face side of the board to peel away from the larger piece. The force was increased until the two board pieces came completely apart. The face surface of the larger piece was then examined to determine on what percentage of its surface the face paper had pulled completely away from the core (referred to as "clean peel"). This percentage is reported in TABLE 8 as the "% Bond Failure".

15

**TABLE 8**  
**Production Line Gypsum Board Paper Bond Failure**

	HI-BOND Concentration (weight %)	STMP Concentration (weight %)	PCF1000 Concentration (weight %)	% Bond Failure (%)
5	0.60	0	0	87
	0.60	0.08	0	97
	0.96	0.08	0	97
	0.60	0.08	0.16	42
10	0.60	0.08	0.32	0
	0.28	0.08	0.32	20
	0.60	0	0	83

The data in TABLE 8 show that in regard to the problem of paper-to-core bond failure after extremely wet conditioning: STMP aggravates the problem; increasing the concentration of typical non-pregelatinized starch (HI-BOND) does not alleviate the problem; adding some pregelatinized starch (PCF1000) alleviates or eliminates the problem.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it should be appreciated that variations and modifications can be effected within the spirit and scope of the invention.

What is claimed is:

1. A method for producing a set gypsum-containing product having increased strength, rigidity, and dimensional stability, comprising:
  - 5 forming a mixture of calcined gypsum, water, and trimetaphosphate ion, and maintaining the mixture under conditions sufficient for the calcined gypsum to convert to set gypsum.
  - 10 2. The method of Claim 1, wherein the concentration of trimetaphosphate ion in the mixture is from about 0.004 to about 2.0 percent by weight, based on the weight of the calcined gypsum.
  - 15 3. The method of Claim 1, wherein the concentration of trimetaphosphate ion in the mixture is from about 0.04 to about 0.16 percent by weight, based on the weight of the calcined gypsum.
  - 20 4. The method of Claim 1, wherein the concentration of trimetaphosphate ion in the mixture is about 0.08 percent by weight, based on the weight of the calcined gypsum.
  5. The method of Claim 1, wherein the trimetaphosphate ion is provided by dissolving a trimetaphosphate salt in the water in the mixture.
  - 25 6. The method of Claim 1, wherein the trimetaphosphate ion is provided by dissolving sodium trimetaphosphate in the water in the mixture.

7. The method of Claim 1, wherein the calcined gypsum comprises beta calcium sulfate hemihydrate.

5        8. The method of Claim 1, wherein the mixture further comprises a pregelatinized starch.

10      9. The method of Claim 1, wherein: the set gypsum-containing product is a gypsum board comprising a core of material sandwiched between cover sheets, wherein the core comprises set gypsum; and the board is formed by depositing the mixture of calcined gypsum, water, and trimetaphosphate ion between the cover sheets and allowing the resultant assembly to set and dry.

15      10. The method of Claim 9, wherein the mixture further comprises a pregelatinized starch.

20      11. The method of Claim 10, wherein the concentration of the pregelatinized starch in the mixture is from about 0.08 to about 0.5 percent by weight, based on the weight of the calcined gypsum.

12. The method of Claim 10, wherein the concentration of the pregelatinized starch in the mixture is from about 0.16 to about 0.4 percent by weight, based on the weight of the calcined gypsum.

25      13. The method of Claim 10, wherein the concentration of the pregelatinized starch in the mixture is about 0.3 percent by weight, based on the weight of the calcined gypsum.

14. The method of Claim 9, wherein: the core has voids uniformly distributed therein; and the mixture further comprises an aqueous foam.

5        15. The method of Claim 14, wherein the aqueous foam has been formed from a foaming agent, or a blend of foaming agents, having the formula



10      wherein X is a number from 2 to 20, Y is a number from 0 to 10 and is 0 in at least 50 weight percent of the foaming agent or blend of foaming agents, and M is a cation.

16. The method of Claim 15, wherein Y is 0 in from 86 to 99 weight percent of the foaming agent or blend of foaming agents.

15      17. The method of Claim 9, wherein the mixture further comprises a pregelatinized starch and an aqueous foam.

20      18. The method of Claim 1, wherein: the set gypsum-containing product is a composite board comprising set gypsum and a reinforcing material; the mixture further comprises the reinforcing material; and the board is formed by depositing the mixture onto a surface and allowing the mixture to set and dry.

25      19. The method of Claim 1, wherein: the set gypsum-containing product is a composite board comprising set gypsum and host particles, at least a portion of the set gypsum being positioned in and about accessible voids in the host particles; the mixture further comprises the host particles, and at least a portion of the calcined gypsum in the

mixture is in the form of crystals in and about the voids of the host particles; and the board is formed by depositing the mixture onto a surface and allowing the mixture to set and dry, whereby the portion of the set gypsum in and about the accessible voids in the host particles 5 forms by *in situ* hydration of the calcined gypsum crystals in and about the voids of the host particles.

20. The method of Claim 1, wherein: the set gypsum-containing product is a machinable material, and the mixture further comprises a 10 starch and particles of a water-redispersible polymer.

21. The method of Claim 1, wherein: the set gypsum-containing product is a material employed to finish a joint between edges of gypsum boards; the mixture further comprises a binder, a thickener, and a non-leveling agent; and the material is formed by inserting the mixture into the 15 joint and allowing the mixture to set and dry.

22. The method of Claim 1, wherein: the set gypsum-containing product is an acoustical tile; the mixture further comprises a gelatinized 20 starch and mineral wool; and the tile is formed by casting the mixture into a tray and allowing the mixture to set and dry.

23. The method of Claim 1, wherein: the set gypsum-containing product is an acoustical tile; the mixture further comprises a gelatinized 25 starch, expanded perlite particles, and a fiber reinforcing agent; and the tile is formed by casting the mixture into a tray and allowing the mixture to set and dry.

24. A composition, useful for producing a gypsum board, comprising a mixture of: water; calcined gypsum; trimetaphosphate ion; and a pregelatinized starch.
- 5           25. A composition, useful for producing a gypsum board, comprising a mixture of: water; calcined gypsum; trimetaphosphate ion; and an aqueous foam.
- 10          26. The composition of Claim 25, wherein the mixture further comprises a pregelatinized starch.
- 15          27. A composition useful, when mixed with water, for producing a composite board comprising set gypsum and host particles, at least a portion of the set gypsum being positioned in and about accessible voids in the host particles, wherein the composition comprises a mixture of: the host particles having the accessible voids therein; calcined gypsum, at least a portion of which is in the form of crystals in and about the voids in the host particles; and a water-soluble trimetaphosphate salt.
- 20          28. A composition useful, when mixed with water, for producing a machinable set gypsum-containing material, comprising a mixture of: calcined gypsum; a water-soluble trimetaphosphate salt; a starch; and particles of a water-redispersible polymer.
- 25          29. A composition useful, when mixed with water, for finishing joints between edges of gypsum boards, comprising a mixture of: calcined gypsum; a water-soluble trimetaphosphate salt; a binder; a thickener; and a non-leaving agent.

30. A composition, useful for producing an acoustical tile, comprising a mixture of: water; calcined gypsum; trimetaphosphate ion; a gelatinized starch; and mineral wool.
- 5           31. A composition, useful for producing an acoustical tile, comprising a mixture of: water; calcined gypsum; trimetaphosphate ion; a gelatinized starch; expanded perlite particles; and a fiber reinforcing agent.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 98/15874

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C04B28/14 C04B22/16

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 681 998 A (US GYPSUM CORP) 15 November 1995 see examples 2-4 ---	1,24
A	DATABASE WPI Section Ch, Week 7830 Derwent Publications Ltd., London, GB; Class L02, AN 78-54041A XP002085465 & JP 53 067720 A (ASAHI DOW LTD) , 16 June 1978 see abstract ---	1,24
A	US 3 297 601 A (UNITED STATES GYPSUM CO) 10 January 1967 see column 5; claim 1 ---	10,24, 28,30,31 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/15874

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 920 465 A (BURKARD EDWARD A ET AL) 18 November 1975 see column 2 - column 3; claim 1 ----	20,28
A	US 4 183 908 A (ROLFE RICHARD B) 15 January 1980 see column 3; claim 1 ----	1
A	US 4 043 825 A (MULLER MARTIN ET AL) 23 August 1977 see examples 2,4 ----	1
A	US 3 347 627 A (MONSANTO CO) 17 October 1967 see column 1, line 19 - line 25; claim 1 -----	1

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